

Determining the kinetics of sunflower husks using dilute acid hydrolysis in the production of furfural

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Abstract:

Laboratory-scale preparation of furfural from sunflower husk was carried out in an attempt to create value-added products from sunflower husk, which has become a source of air pollution in oil mills of India due to burning in boilers. Acid hydrolysis of sunflower husks was performed under varied dilute acid concentrations (1.0–4.0 wt%), reaction temperatures ranging between 150°C and 180°C and the reaction time up to 60 min. The conversion of hemicelluloses into furfural was explored. The maximum furfural recovery 29.8 wt% was obtained at 30 min with 4.0 wt% acid concentration at 170°C. Furfural obtained was characterized using spectroscopic techniques of Fourier Transform Infra-red (FTIR). IR spectrum exhibited a very strong absorption at 1682.95 cm⁻¹, indicating the presence of the conjugated carbonyl (C=O) group. The presence of the aldehyde was proven by two peaks attained at 3262.70 cm⁻¹ and 2,974.33 cm⁻¹. The experimental data were fitted into a kinetic model based on irreversible pseudo-first-order kinetics. The model was successfully validated using the F-test & regression Statistics..

Keywords: Arrhenius parameters; hemicellulose; kinetic model; acid hydrolysis; sunflower husks; furfural

1.Introduction

To increase agricultural economy of India, agricultural residues are used as precursors for the production of bio-gas, bio-oil value-added chemicals, and biochar fuels. Sunflower seeds are the third largest source of crop oil worldwide after soybean and palm (Vaithanomsat P,et.al ,2009). In India domestic production of edible oils in 2016-17 is 10.97 MT which is more than the actual production last year in 2015-16 (i.e. 9.18 MT). (Source: Directorate of Vanaspati, Vegetable oil and Fats (DVVOF))

The increase in demand for vegetable oil led to an increase in the production of sunflower seeds between 10 and 20% annually worldwide. India's share in global production of sunflower oil in 2016-17 may be around 1.0 percent.(Source: United States Department of Agriculture)

Sunflower hulls or husks are the waste of de-hulling, which is a significantly important step for the process economics because removal of hulls leads to a higher pressing capacity, i.e., quantity of oil will more after extraction process (Campbell EJ. ,1983). Centrifugal or pneumatic shellers are used to generate mechanical action to break seeds (Grompone MA.,2005). Due to low bulk density of Sunflower husks their transportation and storage on site is deemed costly and impractical. So it can be transported off-site for composting, as a bedding material, fuel, or low quality roughage for livestock (Dorrell DG.,1976). The sunflower seed husks represent the first valuable waste resulting from the sunflower oil production process following the shelling operation. The husks' content of the processed seeds can reach 22-27%. Seed husks were considered an attractive lignocellulosic source for second generation ethanol production and value added chemicals to improve the overall economics of oil mills. Husks are a lignocellulosic material contained of cellulose, hemicellulose, lignin and ash-forming inorganics. Among several different ways to pretreat biomass, such as dilute acid, alkaline and steam pretreatment, using dilute acids is generally considered the most efficient and a relatively economical (Saha BC, Iten LB,2005) method.

Although several studies have been conducted on pretreatment of sunflower husks and stalks using dilute acid and alkali (Sharma SK, 2004; Kamireddy SR, 2012), none of studies have been performed to optimize the production of xylose and furfural. The objective of this work was to carry out a kinetic study of acidic hydrolysis in sunflower husks using a batch reactor. The results of this study can be used in practical applications if pilot scale batch reactors are set up next to oil mills, in order to increase their overall economic feasibility.

2 Materials and methods

2.1 Source of sunflower husks

The sunflower husks used for the study was procured from local farmers from cultivated land of Akola District, India. All the chemicals and of analytical grade were used. The biomass was air-dried in an open space (average temperature of 35 ± 2 °C) for one day (8 hr per day). Sunflower husk was dried in the oven at 105°C for 7 to 8 hours & then grinded in mixer and screened through 1.1 mm particle size. Moisture content of the raw sunflower husks was determined by oven drying .It was around 6 wt%.

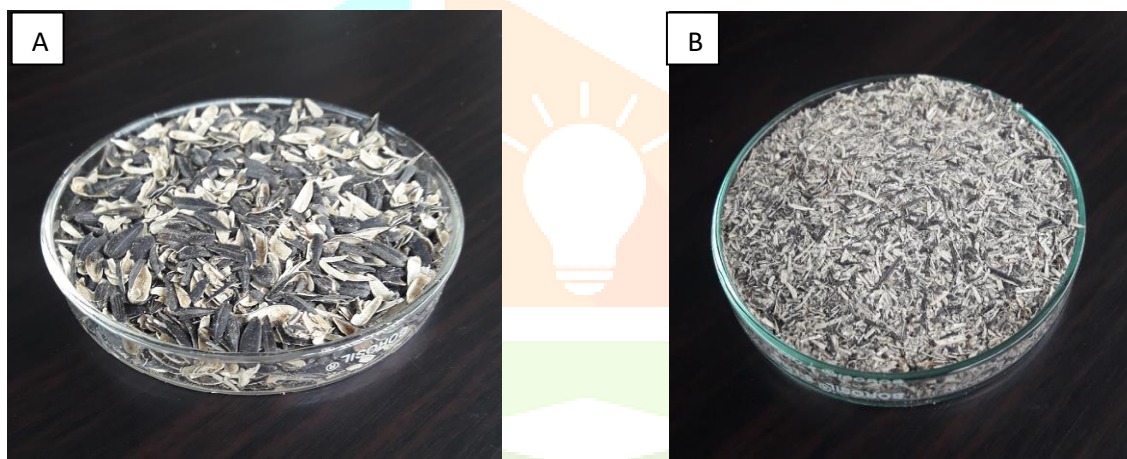


Fig.1 Raw biomass before and after size reductions unscreened Sunflower husk (A), screened Sunflower husk (B)

2.2 Compositional analysis

In a typical composition analysis sunflowers husks contain about 29 wt. % of hemicelluloses, 49 wt. % cellulose, 20 wt% of lignin & 2 wt% of extractives. (Demirbas, 2002). Cellulose, hemicelluloses, lignin and extractives analysis of Sunflower husk were carried out by using reference of L. Nelson and J. A. Leming (1957) (Monoethanolamine Method) [TAPPI (T 222 om-02), 2006]

2.3 Pretreatment of hulls

The husk pretreatment was performed in a 2000 ml internal volume batch reactor manufactured Smart Automation & Hydropneumatics Pvt Ltd. ,Pune .The reactor was made of special type of steel alloy to mitigate the acidic corrosion at high temperatures. The biomass 50 gm and 45 gm of sodium chloride (NaCl) were mixed together in a big clean basin. Then the mixture was placed in a 2 lit reactor. A volume of 1000ml of 1.0% or 2.0 wt% sulfuric acid, which was prepared by mixing deionized water and sulfuric acid purchased from Loba chemical pvt. Ltd., Mumbai. The heating source used for the reactor was heater coil. The agitation rate in the reactor was maintained constant at 50 rpm throughout the reaction. The stirrer rod is made up of glass material having blade of Teflon material to avoid acid corrosion. Once the desired temperature was

reached, it was maintained constant and the reaction time started from that temperature. For indication of temperature K-type thermocouple was mounted inside the reactor to record the temperature–time history of each experiment. Temperature of reactor was control by controller. The agitator having 1/8 HP capacity and speed range of agitator is 10 to 100 rpm.

According to the report, the described NREL process design uses a temperature of 158°C in a dilute-acid pretreatment batch reactor.(Degenstein J, Kamireddy SR,2011). Large amounts of poorly fermentable oligomers are formed at lower reaction temperatures and acid concentrations, whereas significant further degradation of C₅ products usually occurs under higher severity conditions. Hence, we have chosen to carry out this study between 150°C and 180°C; the operational conditions are listed in Table 1. The acid concentration was varied between 1.0 wt% and 4.0 wt%. Each pretreatment experiment was performed up to a maximum reaction time of 30 min. The liquid hydrolyzate samples were withdrawn every 5 min.

2.4. Separation procedure

Distillate collected from the distillation process was subjected to partitioning using chloroform in separation funnel. Aqueous and non-aqueous layers were obtained. Furfural was isolated from the non-aqueous solution using distillation with temperature not exceeding 40 °C.

2.5. Analytical methods

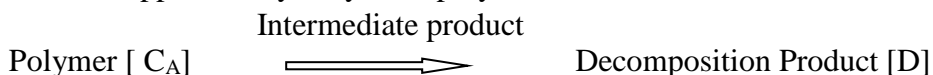
Furfural estimates in hydroxylates: 25ml of each hydroxylate was measured into a conical flask and 20ml of 0.05M potassium bromate/bromide (KBrO₃/BKr) solution added and allowed to stand for five minutes. 10ml of 5% (0.05M) potassium iodine (KI) was then added and the liberated iodine titrated with a standard 0.1M sodium thiosulphate (Na₂S₂O₃ 5H₂O) solution by using starch as an indicator. Then the titre values (volumes of the Na₂S₂O₃ 5H₂O) were recorded. A blank experiment was conducted under the same conditions.

2.6. Identification

FTIR spectrum for the furfural was recorded on Shimatzu FTIR-8400 Spectrophotometer using KBr pellet method. All above analysis was done at UICT, NMU Jalgaon. FT-IR was used for the examination of functional groups of furfural. The spectra were measured between 4000 and 500cm⁻¹. Infrared spectroscopy was carried out using an IR Affinity. Acetone was used as cleaning and diluting agent.

2.7. Kinetic model of acid hydrolysis

Saeman [Saeman JF,1945] kinetic model is applied to hydrolysis of polymeric hemicelluloses. This model is applied to hydrolysis of polymeric hemicellulose and is based on following Eq.



$$K = 1/t \ln (C_{A0}/ C_A) \text{ -----(1)}$$

Where, C_A - the total initial waste hemicelluloses concentration, k - specific rate constant(min⁻¹),

C_{A0} - waste hemicelluloses concentration at time t (g/l) and t , time (min).

The parameters for kinetic study are acid concentration (1-4 wt%) and temperature (130-190 °C) used to investigated a first order rate of furfural formation from sunflower husk hydrolysis by sulfuric acid.

2.8. Calculation of Activation energy

The activation energy of furfural synthesis from sunflower husk is calculated by Arrhenius relationship:

$$\ln K = \ln A - (E_A / RT) \text{ -----(2)}$$

Where K is the rate constant, A is the Arrhenius constant (frequency factor) which is a temperature independent factor, E_A is the activation energy (kJ/mol), R the gas constant (8.314 J/molK) and T is the temperature in Kelvin (K).

2.9. Data analysis for kinetic model

It is necessary to analyze the data using error functions to find out the best model from the goodness of fit with the experimental values. In the present study three different data analysis such as F-test & regression Statistics were used to find out the best fit model to the experimental observations.

3.Results and discussion

3.1 Effect of acid concentration and reaction temperature on furfural yields

Table 1.lists the yield of furfural produced from sunflower husks as a function of time. At 170 °C and 4.0 wt% after 30 min it was found that maximum yield of furfural 29.8 wt%.

Table 1 –Effect of temperature on yield(wt%) of furfural

Acid Concen. Wt %	Reaction Temp. (°C)	Reaction Time (min)				
		0	15	30	45	60
1.0	150	0	0.4	2	1.4	1
2.0	150	0	1.2	3.6	3	2.4
3.0	150	0	4.6	11.4	10.8	10.2
1.0	160	0	3.2	7.8	7	6.4
2.0	160	0	5.8	12.6	11.8	11.4
3.0	160	0	8.4	15.8	15	14.6
1.0	170	0	7.6	9.8	9.2	8.6
2.0	170	0	11.4	15.6	15	14.4
3.0	170	0	19.6	23.2	20.6	20
4.0	170	0	24.2	29.8	26.8	26
5.0	170	0	24.6	29.6	26.4	25.6
4.0	180	0	24.8	29.2	26	25.4
4.0	190	0	24.2	28.8	25.6	25

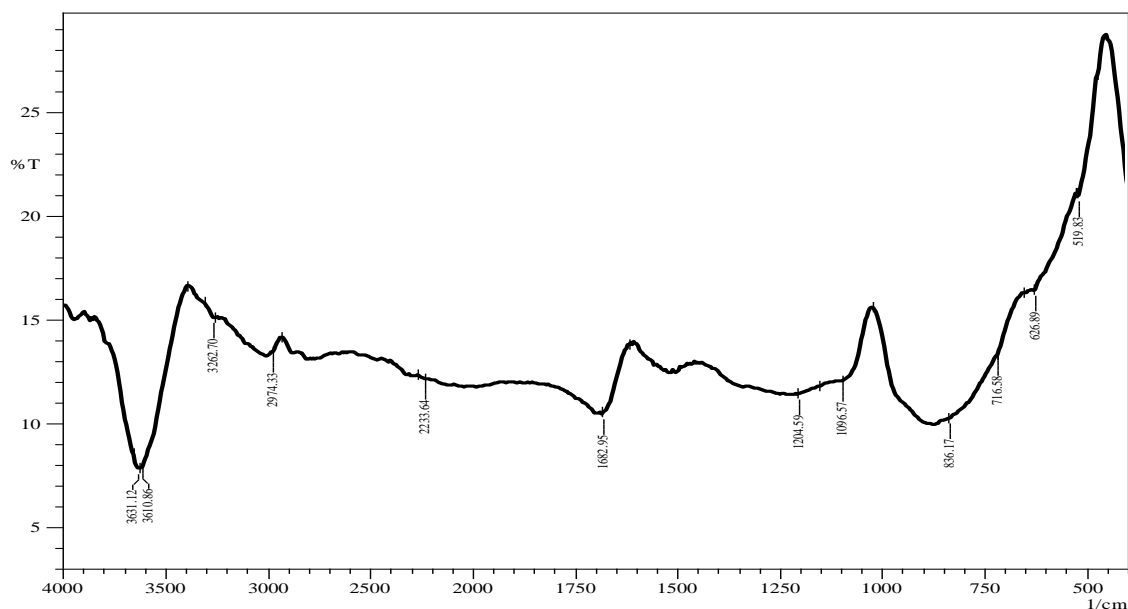


Fig.2: Infrared spectrum of furfural

The IR spectrum (Figure 2) shows a very strong absorption at $1,682.85\text{ cm}^{-1}$. This absorption shows a very significant functional group which is the conjugated carbonyl ($\text{C}=\text{O}$). The absorption wave number is slightly lower than usual i.e. $1,740$ to $1,720\text{ cm}^{-1}$ due to internal hydrogen bonding which occurs in conjugated unsaturated aldehydes. But this peak can appear for chemical compounds like carboxylic acid (COOH), ketone, ester and aldehyde groups. The absence of peak at $1,725\text{ cm}^{-1}$ indicates strongly the presence of aldehyde and not the ketone group (Silverstein and Webster 1998). Furthermore, no broad peaks were observed at the area of $3,400$ to $2,400\text{ cm}^{-1}$ which belongs to the hydroxyl (OH). This confirms the absence of carboxylic acid group. The absorption peak shows strong peaks at 3610.81 & 3631.12 cm^{-1} within the range of 3640 – 3610 cm^{-1} . These absorptions show a moderate intense stretching of $\text{O}-\text{H}$, free hydroxyl & having functional group of alcohols, phenols. Two peaks at 1204.59 and 1096.57 cm^{-1} indicated the $\text{C}-\text{O}$ stretching vibration. This IR spectrum was also compared with the furfural IR spectrum published by M. Sashikala and H.K. Ong (2007)

3.2. Model justification

The best fitted kinetic constant k for the proposed model [Eq. (1)] is listed in Table 2. The rate increased for furfural formation with the increase of reaction temperature and acid concentration, which was also expected based on the literature analysis (Kamireddy S., 2013). Model testing is often performed by comparing the R^2 values obtained by least square fitting; however, exponential kinetic data may be skewed as a result of linearization. Hence an F-test was performed instead, comparing the experimental data with those generated by the theoretical model by varying the pre-exponential factor, activation energy and dimensionless reaction order (Yat SC, Berger A, 2008). Table 4 suggests that the experimental data fitted the model accurately, as the sums of squared errors (SSE) values were low.

Table No.2 -Rate constants at different temperature

Reaction temperature ($^{\circ}\text{C}$)	Rate constant (min^{-1})	Acid concentration (wt%)		
		1	2	3
150	K	1.25×10^{-2}	3.08×10^{-2}	0.2×10^{-2}
160	K	1.69×10^{-2}	5.2×10^{-2}	2.0×10^{-2}
170	K	0.93×10^{-2}	6.5×10^{-2}	16.2×10^{-2}

Table 3 :Fitted Arrhenius parameters [Eq. (2)] obtained using the kinetic constant

kinetic constant	Activation energy, E (kJ/mol)(By graph)
$K = 4.9 \times 10^{-2}$	146

Table No. 4:-F-test of the two sample variance for k rate coefficient for both the experiment and model value

Parameter	K(experimental)	K (Model)
Mean	0.0608272	0.062372
Variance	0.0038981	0.00125062
Observations	11	11
df	10	10
F	3.116931	
P(F<=f) one-tail	0.043605	
F Critical one-tail	2.97823	

The differences between the values of experimental rate coefficients and those generated by the model were low as the sets passed the F-test ($F > F_{\text{critical}}$). Thus, the model applied can be considered suitable, in spite of the integral heterogeneity of the system used. The model was successfully authenticated using the F-test.

Table No. 5: SUMMARY OUTPUT

Regression Statistics	
Multiple R	0.881275478
R Square	0.776646469
Adjusted R Square	0.75182941
Standard Error	0.031103043
Observations n	11

	df	SS	MS	F	Significance F	p value
SSR						
Regression k	1	0.030274628274402	0.030274628	31.29486327	0.000336773	0.099452603
SSE						
Residual	9	0.00870659354377981	0.000967399			0.000336773
SST						
Total	10	0.0389812218181818			alpha=0.077	

If R Square value is 0.77, it means that we are able to explain analysis 77%. Regression value is 01, it means that no. of independent variable is one. The value of Significance F and p-value less than alpha so regression analysis fit for these variables. The value of SSE is low so model is fit.

4. Conclusion

In this study, the effects of sunflower husks acid hydrolysis under varied dilute acid concentrations and reaction temperatures was performed for extraction of pentose carbohydrates and succeeding degradation products. The maximum furfural recovery 29.8 wt% was obtained at 30 min with 4.0 wt% acid concentration at 170°C. It functional groups was identified accurately using FTIR equipments. The experimental data were fitted into a kinetic model based on irreversible pseudo-first-order kinetics. The model was successfully validated using the F-test & regression Statistics. Sunflower husks showed a greater recalcitrance to acid hydrolysis than other agricultural crops, such as kenaf, sorghum and sunn hemp. This difference was explained by a high lignin and wax content of the cell walls, which could act as a barrier to the hydronium ions, resulting in an increase of the activation energy and lowering the effective reaction rate order on the acid.

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